

EFFECT OF CHLOROBENZENE TREATMENT ON THE LOW-SEVERITY LIQUEFACTION OF COALS

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Keywords: Conformational changes, tetralin extraction, hydrogen transfer.

ABSTRACT

Chlorobenzene has the advantage of extracting virtually no organic matter from coals and it has been reported previously, that for the Pittsburgh No. 8 Argonne Premium Coal Sample (APCS), chlorobenzene treatment significantly improved the oil yield as measured by dichloromethane (DCM-solubles) from short contact time hydrogen-donor liquefaction with tetralin (400°C, 15 min.). Similar effects with tetralin have been found for two UK bituminous coals, Point of Ayr and Bentinck, where the yields of DCM-solubles also increased. In contrast, for Wyodak sub-bituminous coal (APCS), pretreatment reduced the yield of DCM-solubles reflecting the vast differences in both liquefaction chemistry and pore structure with bituminous coals. The amounts of hydrogen transferred are broadly similar for the initial and chlorobenzene treated coals strongly suggesting that the improved oil yields arise from limiting char-forming retrogressive reactions rather than cleaving more bonds *per se*. The effect was still evident for Point of Ayr coal when the extraction time was increased from 15 to 60 min., although conversions were considerably higher underlying the importance of the initial contact between coal and solvent. A similar improvement in the oil yield for Point of Ayr coal to that found with tetralin was achieved with hydrogenated anthracene oil which has a boiling range of *ca* 250-450°C and, unlike tetralin, is largely in the liquid phase at 400°C.

INTRODUCTION

Much of the recent literature on the effects of pre-swelling and pre-extracting coals in both polar and non-polar solvents on liquefaction and pyrolysis behaviour⁽¹⁻¹⁰⁾ was briefly reviewed by the authors in an earlier article⁽¹¹⁾. In cases where improved liquefaction yields are achieved, the accessibility of solvents within the highly porous macromolecular structure of coals is undoubtedly improved, particularly during the initial stages of liquefaction where retrogressive reactions need to be avoided. However, unambiguous interpretation of these phenomena in terms of changes in the macromolecular structure of coals is complicated by the fact some organic matter is invariably removed at the same time that conformational changes may be occurring and, in the case of polar solvents and pre-treatments at elevated temperatures, hydrogen bonds are being disrupted. Chlorobenzene has the advantage of extracting virtually no organic matter from coals⁽¹²⁾ but it is non-polar and does not significantly disrupt hydrogen bonds at relatively low temperatures (<150°C). Previous work by one of the authors (PJH)⁽¹³⁾ demonstrated that chlorobenzene treatment markedly

affect mass transfer phenomena in both the Pittsburgh No.8 and Upper Freeport Argonne Premium Coal Samples (APCS) and this prompted an investigation into the effects of the treatment on tetralin extraction and dry hydrogenation (70 bar, with and without a dispersed sulphided molybdenum (Mo) catalyst) for the Pittsburgh No.8 APCS⁽¹¹⁾.

Tetralin was selected because, although it is clearly not representative of process-derived liquefaction solvents as it can be largely in the vapour phase at 400°C, mass transfer effects may be particularly prevalent for this very reason. Further, a relatively short contact time of 15 min. was used as any conformational effects are likely to be most pronounced during the initial stages of conversion. Indeed, the chlorobenzene treatment significantly improved the oil yields as measured by dichloromethane (DCM)-solubles from both tetralin extraction and non-catalytic dry hydrogenation presumably due to improved accessibility of the tetralin and the hydrogen gas. In marked contrast, reduced yields were obtained in catalytic hydrogenation. However, this was probably due to the macromolecular conformation of the coal being further altered by the procedure used for catalyst addition which involved contacting the coal with methanol before drying at ca 100°C.

The yield of pyridine-solubles from the tetralin extraction was also improved by the chlorobenzene treatment. This finding would appear to be contrary to the recent communication by Larsen and co-workers⁽¹⁴⁾ who found that the chlorobenzene treatment reduced the yield of pyridine-insolubles in tetralin for the Illinois No. 6 APCS. However, the extraction was conducted at 350°C where the conversions and level of hydrogen transfer are going to be considerably less than at 400°C. Further, only the yield of pyridine-solubles was determined which is less sensitive than the yield of DCM-solubles to hydrogen utilisation as high conversions to pyridine/quinoline-solubles can be achieved with non-donor polynuclear aromatic compound, such as pyrene for some bituminous coals⁽⁴⁾.

In the continuing investigation into the effects of chlorobenzene treatment on coal conversion phenomena, liquefaction experiments have been conducted on two UK bituminous coals and the Wyodak APCS to address whether the effects of the chlorobenzene treatment found for Pittsburgh No. 8 coal⁽¹¹⁾ are general and, in cases where improved conversions are achieved with hydrogen-donor solvents, whether more hydrogen transferred. Further, are similar effects likely to occur with other hydrogen-donor and non-donor solvents, for example, hydrogenated anthracene oil (HAO) which, unlike tetralin, is largely in the liquid phase at 400°C?

EXPERIMENTAL

The two UK coals, Point of Ayr (87% dmmf C) and Bentinck (83% dmmf C), and the Wyodak APCS were treated in ca 10 g batches with chlorobenzene under nitrogen for 1 week in a Soxhlet apparatus. The treated coals were then dried *in vacuo* at 50°C as were the original coals prior to the liquefaction experiments. For Point of Ayr coal, the treatment was also carried out with the time reduced from 1 week to 3 hours.

The tetralin extractions were conducted in duplicate on the original and chlorobenzene treated samples, using 1 g of coal and 2 g of tetralin at 400°C for 15 min. as described previously⁽¹¹⁾, the yields of DCM and pyridine-solubles being determined. In addition, extractions on Point of Ayr coal were carried out with HAO and naphthalene using the

same conditions and an extraction time of 60 min. with tetralin. The amounts of hydrogen donated to the coals from the tetralin during the extractions were calculated from the gas chromatographic-determined mass ratios of tetralin to naphthalene in the recovered DCM solutions.

RESULTS AND DISCUSSION

Tetralin extractions

Tables 1 and 2 list the yields of DCM-solubles, pyridine-solubles/DCM-insolubles and pyridine-insolubles from the tetralin, HAO and naphthalene experiments. For comparison, the results reported previously for Pittsburgh No. 8 coal are included in Table 1. The duplicate tetralin and naphthalene extractions indicate that the repeatability is $\pm 1\%$ daf coal. The mean values are presented in Figure 1, together with the concentrations of hydrogen donated for the 15 min. extractions.

The results indicate that chlorobenzene treatment has significantly improved the yield of DCM-solubles for the two UK bituminous coals as found previously for Pittsburgh No.8 coal⁽¹¹⁾. Similarly, the yield of pyridine-insolubles for Bentinck coal has also been reduced (Table 1). It would appear that for the 3 bituminous coals investigated, the increase in the yield of DCM-solubles decreases with increasing rank being smallest for Point of Ayr coal (Figure 1). In contrast, the conversions to DCM and pyridine-solubles for the Wyodak APCS have been reduced considerably (Table 1 and Figure 1). This striking difference in behaviour for the one low-rank coal investigated thus far is attributed to the fact that the macromolecular structures of sub-bituminous coals and lignites are swollen to a considerable extent by the water present and its removal during the chlorobenzene treatment and subsequent drying could well lead to a collapse of the pore structure giving much poorer access to hydrogen-donor solvents. Further, the liquefaction chemistry for bituminous and low-rank coals is quite different during the initial stages of conversion, particularly retrogressive reactions involving coupling of dihydric phenolic moieties being more prevalent in low-rank coals⁽¹⁵⁾.

The concentrations of hydrogen transferred during the tetralin extractions are similar for the initial and the treated coals (Figure 1, expressed on a % daf coal basis). This important finding strongly suggests that the improved oil yields are due to changes in the conformational structure of the bituminous coals allowing better solvent access. This limits the extent of char-forming retrogressive reactions rather than cleaving more bonds *per se* which would result in a greater demand for hydrogen. Indeed, the effect is still evident for Point of Ayr coal with an extraction time of 60 min. (Table 1) although the yield of DCM-solubles and the amount of hydrogen donated are considerably higher underlining the importance of the initial contact achieved between the coal and solvent.

Reducing the chlorobenzene treatment time from 1 week to 3 hours had little effect on the conversions indicating that the conformational changes in the macromolecular structure of the coals brought about by the treatment occur on a fast timescale to that of ca 3-7 days usually associated with the removal of low temperature solvent extractable material.

HAO and naphthalene extractions

Table 2 indicates that the effect of the chlorobenzene treatment upon HAO extraction of Point of Ayr coal is similar to that for tetralin with the yield of DCM-solubles increasing by *ca* 10% daf coal. The fact that HAO is largely in the liquid rather than the vapour phase at 400°C suggests that mass transfer limitations on controlling the initial rate of conversion are still severe.

The oil yields obtained with non-hydrogen-donor aromatic compounds, such as naphthalene are obviously much lower than with effective donor solvents and this is reflected in the DCM-soluble yields in Table 2. However, as discussed earlier, aromatic compounds can give high conversions to pyridine/quinoline-solubles (*ca* 80% daf basis) for some bituminous coals⁽³⁾ probably with the aid of hydrogen shuttling or radical mediated hydrogen radical transfer in the case of a number of 4 and 5 ring systems, such as pyrene. Table 2 indicates that the chlorobenzene treatment has reduced the yield of pyridine-insolubles for Point of Ayr coal with naphthalene but has had little effect for the lower rank UK bituminous coal, Bentinck. It was reported previously⁽³⁾ for a different sample of Point of Ayr coal that THF extraction lead to significant improvements in primary conversions to pyridine-solubles with both naphthalene and pyrene. In the case of Bentinck coal, it could well be that the primary conversion is limited by the lack of available hydrogen rather than by solvent accessibility.

General discussion

This investigation has reinforced other recent work⁽¹⁻⁷⁾ which has indicated that pre-treatments can greatly enhance liquefaction yields, particularly in relatively low-severity regimes. However, much of the other work was concerned with pre-swelling coals in polar solvents where the dominant effect is undoubtedly the disruption of hydrogen bonding. The increases in oil yield obtained here of 20-25% upon chlorobenzene treatment for the two bituminous coals of lowest rank (Pittsburgh No.8 and Bentinck) are somewhat greater than that of 14% reported by Joseph⁽³⁾ for tetralin extraction (with a hydrogen over-pressure) of an Illinois No.6 coal pre-treated with tetrabutylammonium hydroxide (TBAH). Increases of only 5% were obtained for THF and methanol but, nonetheless, pre-swelling with both these weakly-basic solvents increased the overall conversions to THF-solubles more than with TBAH. However, their boiling points are considerably lower than that of 132°C for chlorobenzene and, although some disruption of the hydrogen-bonding network in coals would undoubtedly have occurred as the coal swells to a significant extent in these polar solvents, it is uncertain whether the glass transition temperature would have been lowered sufficiently to allow the coal to adopt a lower energy configuration as with chlorobenzene. The nature of the conformational changes have yet to be fully elucidated and are currently being investigated in our laboratory by a combination of DSC, surface area measurements, broadline ¹H NMR and electron microscopy. However, they are clearly different to those induced by polar solvents and could well involve the disruption of non-covalent bonding between aromatic moieties.

There would appear to be considerable scope for improving conversions with process-derived solvents through pretreatments. Although it is clearly impractical to consider the chlorobenzene treatment in terms of a liquefaction process, the fact that it has been shown that the conformational changes can be brought about with a relatively short treatment time (3 hours, Table 1) provides a basis for exploiting such treatments above the glass transition temperatures of bituminous coals with actual process solvents.

ACKNOWLEDGEMENT

The authors thank the British Coal Utilisation Research Association (Contract No. B18) for financial support.

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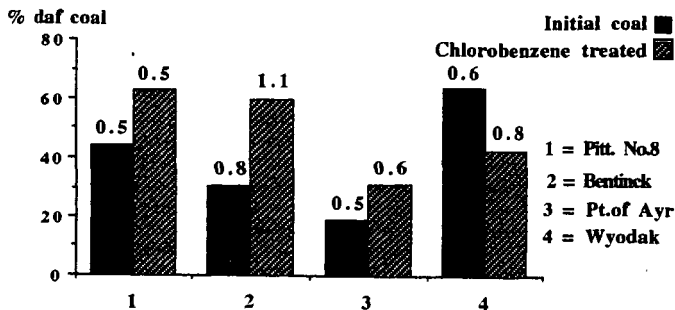


FIGURE 1 YIELDS OF DCM-SOLUBLES FROM TETRALIN EXTRACTIONS INDICATING %H TRANSFERRED (daf BASIS)

Table 1 Tetralin Extraction Results

Coal	DCM-solubles*	% daf coal Pyr sols/DCM-insols	Pyr. insols
<i>Pitt. No.8 (a)(15 min.)</i>			
Initial coal	43.9	52.4	3.7
CB treated coal	62.8	31.0	6.2
<i>Bentinck (15 min.)</i>			
Initial coal	31.5	49.9	18.6
	28.9	46.9	24.4
CB treated coal	59.9	25.2	14.9
	56.6	28.9	14.5
<i>Pt. of Ayr, 15 min.</i>			
Initial coal	18.0	52.9	29.1
	20.1	48.8	31.1
CB treated coal	28.9	27.9	43.2
-one week	33.6	25.1	41.3
-3 hours	29.2	22.3	48.5
<i>Pt. of Ayr, 60 min.</i>			
Initial coal	37.3	36.2	26.5
CB-treated coal	46.7	29.7	23.6

* = 100 - %DCM-insols, includes DCM soluble liquid product + gas + water.

(a) = mean of duplicate runs from ref. 11.

Table 2 HAO and Naphthalene Extraction Results

Solvent/coal (15 min. extraction time)	DCM-solubles*	% daf coal Pyr sols/DCM-insols	Pyr. insols
<i>HAO, Pt. of Ayr</i>			
Initial coal	18.5	31.1	50.4
CB-treated coal	29.9	30.2	39.9
<i>Naphthalene, Pt. of Ayr^(a)</i>			
Initial coal	13.6	15.9	70.5
CB-treated coal	21.0	19.2	57.8
<i>Naphthalene, Bentinck^(a)</i>			
Initial coal	21.7	24.8	53.5
CB-treated coal	22.1	20.6	57.3

(a) = mean of duplicate runs